DISTRIBUTION FUNCTIONS

We work { in the canonical ensemble
{ in the absence of <u>external forces</u> (b)

$P(\bar{R}_1, \dots \bar{R}_N) \equiv$ probability to have ~~probability~~ (probability density) particle 1 in $\bar{R}_1$
particle 2 in $\bar{R}_2$
⋮
particle N in $\bar{R}_N$

IN THE CANONICAL ENSEMBLE

$$P(\bar{R}_1, \dots \bar{R}_N) = \frac{1}{Z} e^{-\beta U(\bar{R}_1, \dots \bar{R}_N)}$$

Z normalizing factor

Now we define [one-particle probability]

$p^{(1)}(R_1)$ probability (density) to have particle 1 in $\bar{R}_1$ <u>IRRESPECTIVE</u> of the positions of the other particles.

We should simply integrate over the positions of the other particles

$$p^{(1)}(R_1) = \frac{1}{Z} \int dr_2 \dots dr_N \, e^{-\beta H(R_1, r_2, r_3 \dots r_N)}$$

$p^{(2)}(R_1, R_2)$ probability (density) to have particle 1 in $\bar{R}_1$ and particle 2 in $\bar{R}_2$, irrespective of the positions of the other particles

$$P^{(2)}(R_1, R_2) = \frac{1}{Z} \int dr_3 \dots dr_N \, e^{-\beta H(R_1, R_2, r_3 \dots r_N)}$$

DEFINITION:

$$g^{(2)}(R_1, R_2) = \frac{P^{(2)}(R_1, R_2)}{P^{(1)}(R_1) P^{(1)}(R_2)}$$

PAIR DISTRIBUTION FUNCTION

Such a quantity gives the correlations among the positions of the particles

SOME LIMITING CASES:

(a) ideal gas

particle do not interact.

The probability to have two particles in $\bar{R}_1$ and $\bar{R}_2$ is simply the product of the one-particle probabilities

$$P^{(2)}(R_1, R_2) = P^{(1)}(R_1) P^{(1)}(R_2) \Longrightarrow g^{(2)}(R_1, R_2) = 1$$

(b) large distances

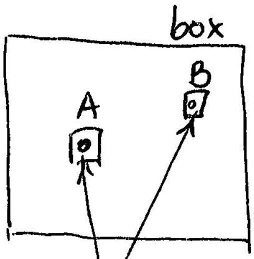
We only consider SHORT-RANGE INTERACTIONS

If the distance between the two particles is much larger than the interaction range the two particles do not influence each other

Again, there is factorization

$$g^{(2)}(R_1, R_2) \approx 1 \quad \text{for } |R_1 - R_2| \text{ large}$$

The absence of external forces implies that the system is <u>HOMOGENEOUS</u> (apart from the region close to the boundaries

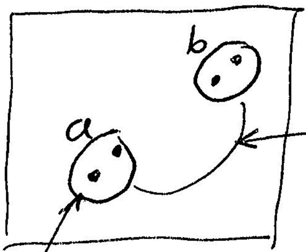


The probability to be in A and B is the same

$\downarrow$

$p^{(1)}(R)$ does not depend on R (boundary effects are negligible)

$\downarrow$



the two configurations are obtained by using a rigid translation

The probability of the 2-particle configuration in a is the same as that in region b

$\downarrow$

$p^{(2)}(R_1, R_2)$ depends only on $\bar{R}_1 - \bar{R}_2$

$$p^{(1)}(R) = \frac{1}{V} \quad \text{because} \quad \int_{\text{box}} d\vec{R}\, p^{(1)}(R) = 1$$

It follows that $g^{(2)}(R_1, R_2)$ is only a function of $\bar{R}_1 - \bar{R}_2$

$$g^{(2)}(R_1 - R_2) = V^2 p^{(2)}(\bar{R}_1, \bar{R}_2)$$

Finally

$$p^{(2)}(\bar{R}_1,\bar{R}_2) = \frac{1}{Z}\int dr_3 \dots dr_N \, e^{-\beta U(R_1,R_2,r_3\dots r_N)}$$

$$= \frac{1}{Z}\int dr_1 \dots dr_N \, \delta(r_1-R_1)\,\delta(r_2-R_2)\,e^{-\beta U(r_1 \dots r_N)}$$

$$= \langle \delta(\bar{r}_1-\bar{R}_1)\,\delta(\bar{r}_2-\bar{R}_2) \rangle$$

So that

$$g^{(2)}(R_1-R_2) = V^2 \langle \delta(\bar{r}_1-R_1)\,\delta(\bar{r}_2-\bar{R}_2)\rangle$$

Now change variable

$\bar{R}_{12} = \bar{R}_1 - \bar{R}_2$ relative position

$\bar{R}_{CM} = \frac{1}{2}(R_1+R_2)$ center-of-mass position

obtaining

$$g^{(2)}(R_{12}) = V^2 \langle \delta(\bar{r}_1 - R_{CM} - \frac{R_{12}}{2})\,\delta(r_2 - R_{CM} + \frac{R_{12}}{2})\rangle$$

Now, we average over $\bar{R}_{CM}$

$$g^{(2)}(R_{12}) = \frac{1}{V}\int d^3\bar{R}_{CM}\, g^{(2)}(R_{12}) =$$

$$= V \int d^3\bar{R}_{CM} \langle \delta(\bar{r}_1 - R_{CM} - \frac{R_{12}}{2})\,\delta(r_2 - R_{CM} + \frac{R_{12}}{2})\rangle$$

the δ-function implies $R_{CM} = r_1 - \frac{R_{12}}{2}$

$$= V \langle \delta(r_2 - r_1 + \frac{R_{12}}{2} + \frac{R_{12}}{2})\rangle =$$

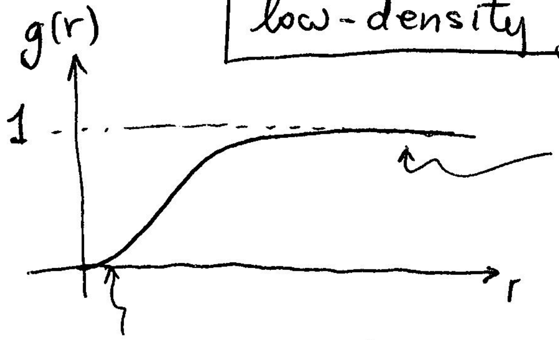
$$= V \langle \delta(r_2 - r_1 + R_{12})\rangle = V \langle \delta(\bar{r}_1 - \bar{r}_2 - \bar{R}_{12})\rangle$$

Note that homogeneity also implies that $g^{(2)}(R)$ is only a function of $|\vec{R}|$, the distance between the two particles.

Typical graphs of $g^{(2)}(r)$

r: scalar variable : distance

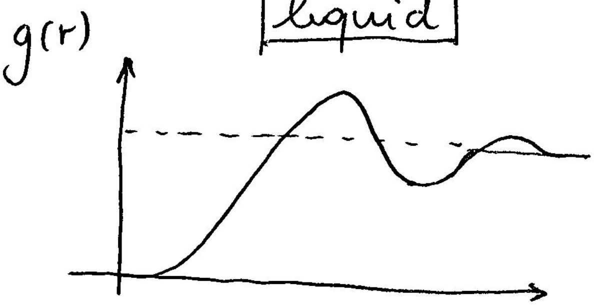
low-density gas



for $r \gtrsim$ a few interaction length scales it goes to 1

for r small it vanishes : the probability to have two particles in the same position is zero

liquid



The presence of oscillations indicates the presence of short-range order : There are preferred distances for the molecules.